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Mechanism of 6H-3C transformation in SiC

S.I. Vlaskina

Institute of Semiconductor Physics, NAS of Ukraine, 45 prospect Nauky, 03028 Kiev, Ukraine

Phone: +380(44) 269 3792; fax +380(44) 265 8342; e-mail:businkaa@mail.ru

Dong Seoul College, 461-714, 423,

Bokjung-Dong, Sunnam- city, Kyonggi-do, Korea

Phone: 82(031)7202141; fax 82(0342)7202261; e-mail:svitlana@haksan.dsc.ac.kr

Abstract. Heavily doped by nitrogen single crystals of 6H-SiC were completely transformed into 3C-SiC ones by annealing in vacuum at presence of Si vapor for 1 hour at 2180 K or 4 hours at 2080 K. Mechanism of solid-to-solid transformation have been studied. Calculated nitrogen concentration from the Hall effect and EPR spectra for transformed crystals show its decreasing value in 3C-SiC. Data show appearance of new defects – donors and acceptors – that make nitrogen optically and electrically non-active. These defects accompany the process of transformation.

Keywords: silicon carbide, phase transformation.

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1. Introduction

Many attempts have been made to explain polytypism in SiC, ZnS, CdJ₂. The transformation from one polytype to another takes place in gas phase [1-2] or in solid state [3-4] and can be considered both from thermodynamic and kinetic points of view. In most experiments dealing with polytypism, β -SiC (cubic phase) has been reported to transform to α -SiC (hexagonal phase), in particular the 6H phase, by high-temperature annealing. Many authors have studied these $\beta \rightarrow \alpha$ transformations in SiC. In general, the 6H polytype is stable at high temperatures, while 3C-SiC at low ones. A few reports of the “reverse” transformation, i.e., 6H \rightarrow 3C, confirmed their realization even at high temperatures. A number of these transformations have been made under high nitrogen pressures and at high temperatures in hard nitrogen doped Lely crystals. The authors concluded that nitrogen stabilized the 3C polytype at high temperatures. In general impurities are believed to have an important influence on the stability of different polytypes of SiC. Acceptor impurities, such as B or Al, are reported to stabilize layers in a hexagonal environment, while donor impurities, such as N or P, stabilize layers in a cubic environment. Actual mechanism of polytypic transformation in solid state as a kinetic problem has been considered both as diffusive

process and dislocation processes. The present paper discusses some possibilities of 6H-3C transformation and transformation mechanism.

2. Experimental results and discussion

Hard dark green heavily nitrogen doped 6H-SiC samples (concentration of donors nitrogen Nd-Na about 10^{19}cm^{-3}) with thickness about 500 μm were transformed partly or fully at 3C-SiC by the method described in [5]. Heavily nitrogen doped 6H-SiC crystals were exposed to 1500-2500 K temperature at the presence of Si vapor in vacuum crucible. After the transformation process, crystals became yellow, thinner (100-200 μm) and not transformed part of initial 6H-SiC that became white or even slightly violet. The crystals are completely transformed into 3C-SiC when 6H-SiC is annealed for 1 hour at 2180 K or 4 hours at 2080 K. The quantity of transformed 6H \rightarrow 3C SiC was calculated using phase-contrast microscope for crystals annealed for various times at different temperatures. Fig. 1a shows the content of 3C-SiC in 6H-SiC phase (η) versus temperature. The content of 3C-SiC (in %) was calculated as a ratio of transformed area to common area using photos of crystals heated at different temperatures for the same time ($t = 1$ hour).

According with Avraami-Kolmogorov equation:

$$\eta = 1 - \exp(-kt^n) \quad (1)$$

Usually “n” value shows a mechanism of transformation. From the kinetic of transformation (Fig. 2b) “n” is close to 3 (n=3) in our case.

$$\eta = 1 - \exp\left(-\frac{1}{3\pi}t^3 \cdot V_{cr} \cdot V_{gr}^3\right) \quad (2)$$

V_{cr} – velocity of nuclear creation,
 V_{gr} – velocity of nuclear growth.

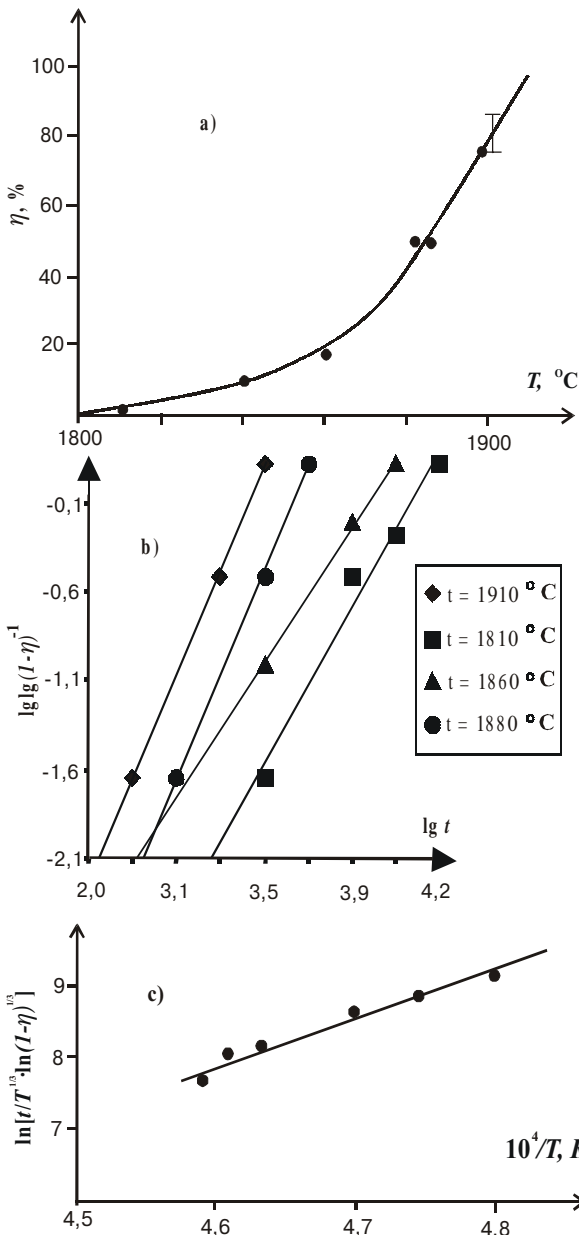


Fig. 1. a – Temperature dependence of 3C-SiC content in 6H-SiC phase, b – calculation of “n”, c - activation energy.

Creation of crystallization centers is necessary for a crystallization process.

The velocity of this creation is as follows:

$$V_{cr} = c_1 \cdot e^{-\frac{W}{kT}} \quad (3)$$

where:

W – activation energy for new nucleus creation,
 k – the Boltzmann constant,
 T – temperature.

The velocity of new phase creation is constant.

The velocity of a new phase growth is:

$$V_{gr} = c_2 \cdot v \cdot e^{-\frac{U}{kT}} \quad (4)$$

U – average activation energy of self-diffusion of new and old phases.

Characteristic frequency:

$$\eta = 1 - \exp(-kt^n) = 1 - \exp\left(-\frac{1}{3\pi}t^3 \cdot V_{cr} \cdot V_{gr}^3\right) \quad (5)$$

$$\eta = 1 - \exp\left(-C \cdot T \cdot e^{-\frac{W}{kT}} \cdot e^{-\frac{3U}{kT}} \cdot t^3\right) \quad (6)$$

$$1 - \eta = \exp\left(-C \cdot T \cdot t^3 \cdot e^{-\frac{W}{kT}} \cdot e^{-\frac{3U}{kT}}\right) \quad (7)$$

$$\ln(1 - \eta) = -C \cdot T \cdot t^3 \cdot \exp\left(-\frac{W}{kT}\right) \cdot \exp\left(-\frac{3U}{kT}\right) \quad (8)$$

$$\frac{-\ln(1 - \eta) \cdot \exp\frac{W}{kT} \cdot \exp\frac{3U}{kT}}{C \cdot T} = t^3 \quad (9)$$

Transformation activation energy was calculated according:

$$t = B \cdot [-\ln(1 - \eta)]^{\frac{1}{3}} \cdot T^{-\frac{1}{3}} \cdot \exp\left(\frac{W + U}{kT}\right) \quad (10)$$

$$\frac{U + \frac{W}{3}}{kT} = \ln \frac{t}{B \left[-\ln(1 - \eta)\right]^{\frac{1}{3}}} \quad (11)$$

From Fig. 1c:

$$\left(U + \frac{W}{3}\right) = 140 \pm 20 \text{ Kcal / mol.} \quad (12)$$

This calculated activation energy is very close to the energy of sublimation.

This calculation was based on the assumption of creation of new centers providing both crystallization and growing processes of these centers. It means that it is based on solid-state transformation going on with new phase-disordered 6H-SiC structure and through formation of an intermediate multilayer structure. Fact of closing this energy to the gas transformation energy shows the similar nature of both processes.

A possible model of this transformation is a site changing according to $A \rightarrow B$, $B \rightarrow C$ or $C \rightarrow A$ and changing stacking sequence ABCACB (6H-SiC) to ACB (3C-SiC) followed by final 6H \rightarrow 3C conversion through formation of an intermediate multilayer structure. It can be both a diffusion process and the dislocation one.

As seen from the Hall effect measurements, free carrier concentration at $T = 300$ K (noncompensated impurities $-N_d - N_a$) became 10^{15} cm^{-3} , that is decreased by three orders of magnitude. The mobility was increased. In some very small transformed 3C crystals, mobility was $790 \text{ cm}^2/\text{V}\cdot\text{s}$, free carrier concentration $6.1 \cdot 10^{16} \text{ cm}^{-3}$, conductivity $7.75 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. Some samples had mobility $960 \text{ cm}^2/\text{V}\cdot\text{s}$.

Several samples had very high resistivity (conductivity about $6 \cdot 10^{-3} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ and less), and we could not make measurements.

In general, it is necessary to do the Hall measurements only at one plane of originally grown 3C-SiC crystals because the concentration and all parameters are different at available planes due to differing velocities of the crystal growth in various directions and at different nitrogen doping. But we could not make such measurements using transformed crystals. In Fig. 2, shown are the results of Hall measurements in transformed crystals (temperature dependences of the free carrier concentration).

Temperature dependence of mobility is shown in Fig. 3. Some deep donor levels at $0.35 \pm 0.1 \text{ eV}$ and $0.74 \pm 0.04 \text{ eV}$ appear in the crystal. Usual nitrogen levels are about 0.1 eV . In Fig. 2 black points are experimental, and another ones theoretically calculated for a two-level system. Lines 1 and 2 are indicative of this fact. Deep level 0.35 eV appears at low temperatures only. At temperatures close to 400 K this level is exhausted, and free carrier concentration is $2 \cdot 10^{17} \text{ cm}^{-3}$. Compensation of this level is very small (about 1% as it was calculated accordingly to equation for doped and compensated semiconductors). New deep levels (0.74 eV) appear at 400 K . The concentration of these levels is very high. The temperature dependence of mobility (Fig. 3) shows some material property improvement and argues in favour of absence of new scattering centers. But, in general, the mobility is increased.

The nitrogen concentration calculated from EPR spectra for transformed crystals shows a decreasing nitrogen concentration in 3C-SiC.

All these data show appearance of new defects - donors and acceptors that make nitrogen optically and electrically non-active. These can be vacancies (Si-vacancy - as an acceptor, C-vacancy - as a donor or more compli-

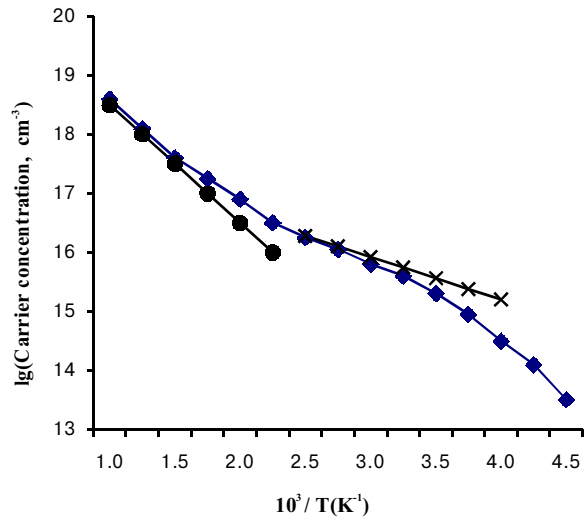


Fig. 2. Temperature dependence of the free electron concentration.

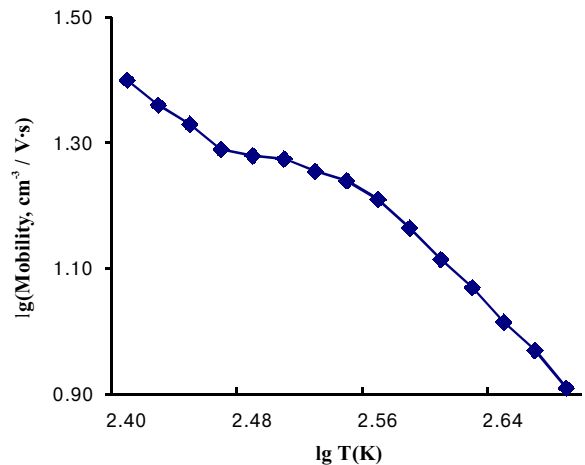


Fig. 3. Temperature dependence of the free electron mobility.

cated complexes, namely: nitrogen-vacancy, vacancy-vacancy, or some impurities play more important role in these processes). Nature of these defects has to be understood later - now we don't know it exactly. But these defects accompany processes of transformation.

3. Conclusion

So, 6H \rightarrow 3C transformation in SiC was investigated as a solid-state transformation. Tight proximity of meanings valid for the transformation and sublimation energies as well as for the gas phase transformation one enabled us to consider this 6H \rightarrow 3C conversion as accompanied by

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some reconstruction processes. At the same time, it is clear that some new defects participate in these processes. Probably, these defects are complexes of doping elements with silicon and carbon vacancies. And vacancies play an important role in the transformation process. Some electrical properties were investigated, too.

References

1. A.J. Verma, P.Krishna, Polymorphism and Polytypism in Crystals, Wiley, New York, (1966).
2. P.Krishna., R.C. Marshall, Direct transformation from the 2H to the 6H-structure in single crystal SiC// J.Cryst.Growth, **9**, pp.310-327 (1971).
3. H.Yagodzinsky, Polytypism in SiC crystals// Acta crystals, **7**, pp.300-307 (1954).
4. J.W. Yang, P.Pirous, The aOb polytypic transformation in high-temperature indented SiC// J.Mater.Res, **8** (11), pp.2902-2906 (1993).
5. Vlaskina S., Shin D.H. 6H to 3C Polytype transformation in Silicon Carbide// Jpn.J.AppI.Phys. **38**(1A), pp.L27-L29 (1999).